Single-crystal, Vacuum-ultraviolet, and Ion-association Circular-dichroism Spectra of the Bis[(2*R*)-2-methyl-1,4,7-triazacyclononane]cobalt(III) Ion

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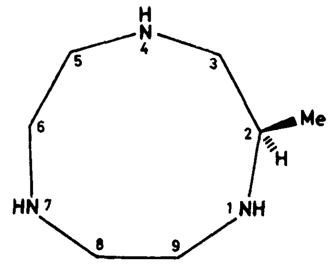
The circular dichroism (c.d.) spectrum of a single crystal of $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]I_3.5H_2O$ [(2*R*-Me)-tacn = (2*R*)-2-methyl-1,4,7-triazacyclononane] with radiation propagated along the crystal *c* axis is compared with that of the corresponding perchlorate salt in aqueous solution, the latter spectrum being extended into the vacuum u.v. region. The comparison indicates that the rotational strengths of the D_3 components of the *d*-electron transition to the octahedral $^1T_1$ state of the $Co^{III}N_6$ chromophore at 476 nm make the relative contribution $|R(A_2)| > |R(E)|$ to the optical activity, in contrast to the converse inequality found in the tris(diamine)cobalt(III) series. The contrasting inequalities are correlated with the predominant location of ligand groups in the polar and in the equatorial D_3 region for the title complex and for the tris(diamine)cobalt(III) series, respectively. The addition of multiply charged oxo-anions to $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]^{3+}$ in solution enhances $R(E)$ at the expense of $R(A_2)$, indicating a preferred equatorial location of the anion in the ion-association structure. Ligand-polarisation calculations of the rotational strengths of chiral $Co^{III}N_6$ complexes with ligand groups in D_3 polar locations, while correct in sign, are not quantitatively satisfactory.

THE present work reports the axial circular dichroism (c.d.) spectrum of a single crystal of bis[(2*R*)-2-methyl-1,4,7-triazacyclononane]cobalt(III) iodide pentahydrate over the 270—550 nm region and solution c.d. studies of the corresponding perchlorate and other salts down to 165 nm. The principal aims of the work are, first, the spectroscopic characterisation of the *d–d* and the charge-transfer (c.t.) optical activity of trigonal $Co^{III}N_6$ complexes owing their chirality mainly to a preferred conformation of the chelate rings and, secondly, an extension of the ligand-polarisation model for *d*-electron rotational strengths from the previously studied series of tris(diamine)cobalt(III) complexes,[1] where the ligand groups have a largely equatorial disposition in the D_3 frame, to chiral trigonal complexes where the corresponding groups have a more polar location. An additional aim is the further characterisation of the preferred mutual steric relationships between the moieties of the ion associations formed by a chiral complex cation and a polarisable anion in solution.

RESULTS AND DISCUSSION

The ligand, (2*R*)-(—)-2-methyl-1,4,7-triazacyclononane, (2*R*-Me)-tacn (1), and the complex $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]^{3+}$ (2), were synthesised[2] with the expectation, from molecular models, that the individual chelate rings of each ligand spanning a triangular face of the co-ordination octahedron in the complex (2) have a common preferred conformation, forming the left-handed (λλλ) conformation set in the case of the ligand (1). The preferred equatorial disposition of the exocyclic methyl group with respect to the mean plane of a propylenediamine chelate ring in complex (2) requires the λ conformation of that ring segment and the two linked ethylenediamine ring units of ligand (1) in complex (2) to adopt the same λ conformation on account of the particular orientation of the bonds to the tetrahedrally co-ordinated nitrogen atoms terminating the propylenediamine chelate ring-segment.

The *X*-ray diffraction study[3] of the crystal and molecular structure of $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]I_3{\cdot}5H_2O$ shows that each of the six chelate rings adopts the λ conformation and that the additional chiral centres introduced into the ligand (1) by co-ordination of the three nitrogen atoms have the configuration (1*S*,4*R*,7*S*). The positions of the exocyclic methyl group of the ligand (1) in complex (2) exhibit orientational disorder in the crystal structure,[3] indicating that the three geometric isomers



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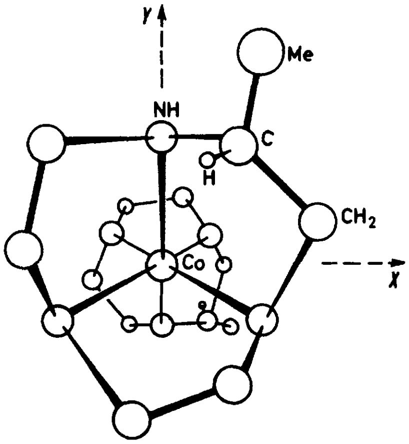


(2)

of the complex with a common bis(1*S*,2*R*,4*R*,7*S*) configuration, and distinguished by the mutual steric relationship of the two methyl groups, are present with equal probability in the crystal.

An alternative co-ordination mode of ligand (1) affords the (1*R*,4*S*,7*R*) configuration at the nitrogen atoms and again each of the three chelate rings formed has the λ conformation, owing to the equatorial preference of the (2*R*)-2-methyl group.[4] Three geometric isomers of complex (2), dependent upon the mutual disposition of the two exocyclic methyl groups, are feasible for each of the three configurationally distinct co-ordination modes of the two ligands (1), *i.e.* both (1*S*,4*R*,7*S*), as in the crystal,[3] or both (1*R*,4*S*,7*R*), or one of each of the two modes.[4] Recently, the nine geometrical and configurational isomers of the cation of (2) have been partly separated into five fractions by chromatography of the complex on a Sephedex column, and the individual fractions have been characterised by n.m.r., i.r., u.v., and c.d. spectroscopy.[4] Fractions representing each of the three configurationally distinguished co-ordination modes of the two ligands (1) in the complex are identified, together with the geometric isomers or mixtures of those isomers, for each co-ordination mode.[4]

The c.d. spectra of all of the isomers of complex (2) isolated are remarkably similar [4] consisting of a major positive band near 480 nm (Δε 4.35—4.77) due to the octahedral $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition of the $Co^{III}N_6$ chromophore, a minor negative band near 430 nm (Δε −0.24 to −0.31), due to the $^1A_1 \rightarrow {}^1T_2$ transition, and a large positive double band in the metal–ligand charge-transfer region 215—250 nm (Δε 10—17). The similarities indicate that the optical activity of this complex is not sensitive to the relative steric relationship of the two exocyclic methyl groups, nor to the co-ordination modes of the nitrogen atoms of the ligand (1), and is primarily dependent upon the particular locations of the ligand groups in the frame of the $Co^{III}N_6$ chromophore, and the distortions from regular octahedral co-ordination of the chromophore, imposed by the λ conformation of all six chelate rings in each of the nine isomers of the complex.

In contrast to the tris(diamine)cobalt(III) complexes, no net dissymmetry results from the mutual skew relationship of the mean planes of pairs of chelate rings in the complex ion (2) and in the geometric and configurational isomers arising from the several co-ordination modes of the ligand (1). The contributions to the chirality from such ring pairs sum to zero over all the pairs in the complex. Design features [2] in the synthesis of complex (2) were the absence of configurational chirality due to the skew relationship of the mean planes of the chelate rings, and the location of the perturbing alkyl groups of the polyamine ligand (1) in spatial regions more remote from the D_3 equatorial plane of the $Co^{III}N_6$ chromophore than in the corresponding tris(diamine) complexes.

In the ligand-polarisation model the alkyl groups of the chelate rings in a D_3 tris(diamine)cobalt(III) complex dominate the *d*-electron optical activity and they are necessarily located in a region close to the equatorial *XY* plane of the complex.[1] A previous assessment of the effect of substituent groups located in the D_3 polar regions, near to the $C_3(Z)$ axis, of a trigonal $Co^{III}N_6$ complex, through a c.d. study of *N*-alkylethylenediamine derivatives,[5] was limited by the superposition of both the ring-conformation and the mean-plane configurational effects, and the predominant perturbation of the $Co^{III}N_6$ chromophore by the methylene groups of the chelate rings located close to the D_3 equatorial plane.

The *X*-ray determination [3] of the molecular structure of complex ion of (2) and its geometric isomers in the crystal $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]I_3 \cdot 5H_2O$ shows that the significant distortions from regular octahedral co-ordination are a polar elongation, expressed by the angle of 51.3° between each Co–N bond and the molecular three-fold rotation axis, compared with the corresponding angle of 54.75° for an octahedral $Co^{III}N_6$ cluster, and a clockwise rotation by 7.6° of the co-ordination triangle of the upper ligand with respect to that of the lower around the C_3 axis of the complex ion.

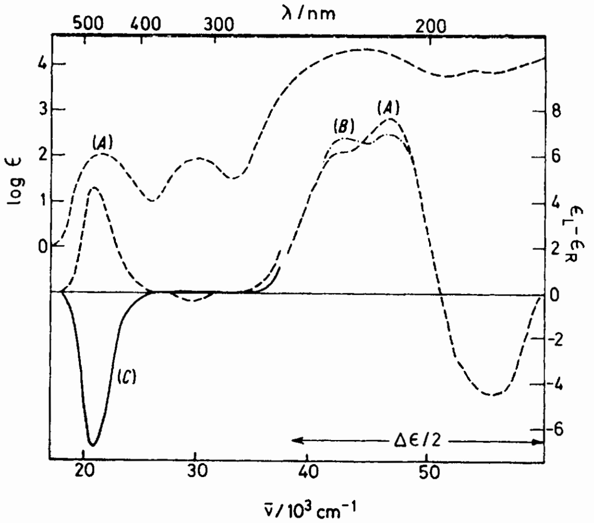


FIGURE 1 The absorption spectrum (upper curve) and c.d. spectrum (lower curve) of $[Co\{(2R\text{-}Me)\text{-}tacn\}_2][ClO_4]_3$ in water, or in D_2O for the 160—260 nm region (*A*), and in methanol (*B*), and the c.d. spectrum of a single crystal of $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]I_3 \cdot 5H_2O$ with radiation propagated along the crystal *c* axis (*C*). Units of ε and Δε = ($ε_L$ — $ε_R$) are dm³ mol⁻¹ cm⁻¹. Similarly in Figure 2

The C_3 axis of each complex ion in (2) is orientated parallel to the *c* axis of the crystal,[3] which belongs to the space group *R*32. Accordingly, the crystal is optically isotropic perpendicular to the *c* axis in the plane parallel to the D_3 equatorial *XY* plane of each complex ion. Radiation propagated along the *c* axis of the crystal retains its incident polarisation and gives rise only to electronic transitions with an electric and magnetic dipole moment directed in the equatorial *XY* plane of the complex, the transitions polarised along the direction of the polar C_3 axis remaining inactive.

The c.d. spectrum of a single crystal of complex (2) with the radiation propagated along the crystal *c* axis is compared in Figure 1 with that of an aqueous solution of the corresponding perchlorate salt. The comparison shows (Table) that, of the two D_3 components of the *d*-electron transition to the octahedral $^1T_1$ state of Co^{III} near 21 000 cm^{-1}, the $^1A_1 \rightarrow {}^1E$ component polarised in the equatorial XY plane of the complex has, from the single-crystal spectrum, a negative and the minor rotational strength [$R(E) = -0.16$ Debye magneton], while the component polarised along the $C_3(Z)$ axis, $^1A_1 \longrightarrow {}^1A_2$, has a positive and the major rotational strength [$R(A_2) = 0.32$ Debye magneton], as is shown by the sum of the two strengths, $R(T_1)$, given by the aqueous solution c.d. spectrum (Figure 1, Table).

TABLE

Experimental and calculated first-order rotational strengths,* in Debye Bohr magneton, of the D_3 components, $R(A_2)$ and $R(E)$, of the octahedral $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition of the $Co^{III}N_6$ chromophore near 21 000 cm^{-1}, and the corresponding sum, $R(T_1)$, for complexes (2) and (3)

Complex		$R(A_2)$	$R(E)$	$R(T_1)$
(2) $[Co\{(2R\text{-Me})\text{-tacn}\}_2]^{3+}$	theor.	0.66	−0.64	0.020
	expt.	0.32	−0.16	0.16
(3) $(-)[Co(sep)]^{3+}$	theor.	−0.32	0.31	−0.010
	expt.			−0.068

* The atomic unit of rotational strength $[h^3/(m^2e^2c)]$ is equivalent to 5.083 Debye Bohr magneton, and to 4.714×10^{-38} e.s. units cm erg G^{-1} (c.g.s. units) or to 1.572×10^{52} C m J T^{-1} (S.I. units). $R(\text{D.B.M.}) = 0.248\int(\Delta\varepsilon/\nu)d\nu$ with $\Delta\varepsilon$ in dm^3 mol^{-1} cm^{-1}.

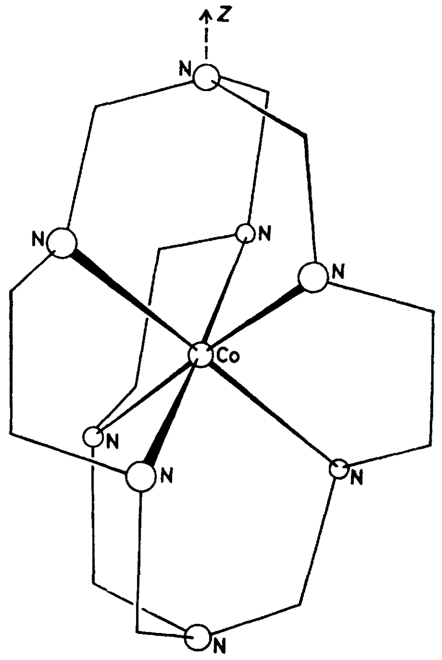
In contrast, single-crystal and solution c.d. studies of the tris(diamine) complexes of Co^{III} show [1,6] that $R(E)$ is generally the dominant rotational strength in complexes containing five-membered chelate rings, governing the sign of the sum, $R(T_1)$, measured for the randomly orientated complex ion in solution, although the disparity between the magnitudes of $R(A_2)$ and $R(E)$ is invariably smaller than is found in the case of complex (2) (Table). Further, $R(T_1)$ for the complex ion in (2) has a value (0.16 Debye magneton) larger than expected from the c.d. spectrum of the (*R*)-(−)-propylenediamine complex,[7] $[Co(NH_3)_4\{(R)pn\}]^{3+}$, on a simple additivity basis, for six five-membered diamine chelate rings each with the λ conformation (0.042 Debye magneton). The linkage of three chelate rings in each of the two macrocyclic ligands (1) in complex (2) produces additional chiral perturbations of the $Co^{III}N_6$ chromophore, which are expressed in the polar elongation and the trigonal twist of the two ligands (1) about the C_3 axis of the complex as determined by the *X*-ray crystal-structure analysis.[3]

The co-ordinates of the atoms heavier than hydrogen in complex (2) obtained in the *X*-ray diffraction study [4] provide a basis for the estimation of the *d*-electron rotational strengths arising from the chiral perturbation of the $Co^{III}N_6$ chromophore, employing the ligand-polarisation model.[1,5] Calculations of the *d*-electron rotational strengths of complex (2) and its geometrical isomers have been carried out, to the first order of perturbation theory, by the method and with the parameters previously described.[1,5]

In the ligand-polarisation model the leading electric multipole moment of each of the three components of the octahedral $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition of Co^{III}, *e.g.* the hexadecapole $H_{xy(x^2-y^2)}$ of the component $d_{xy} \rightarrow d_{x^2-y^2}$ and the analogues obtained by cyclic permutation of the electronic co-ordinates, is assumed to coulombically align the electric dipole moment induced by the radiation field in each of the ligand groups CH, CH_2, CH_3, or NH, dependent upon the particular location of the heavy atom of that group in the co-ordinate frame of complex (2). The magnitude of each induced dipole is taken to be proportional to the mean polarisability of the group considered at the frequency of the electronic transition.

The scalar product of the resulting first-order electric dipole moment with the zero-order magnetic-dipole transition moment ($2^{\frac{3}{2}}$ B.M. for each of the three *d*-electron excitations) * gives the first-order rotational strength. The octahedral components, $d_{xy} \rightarrow d_{x^2-y^2}$ and its analogues, are taken in the appropriate linear combinations, determined group-theoretically, for complexes of lower symmetry. The first-order rotational strengths listed (Table) refer to D_3 symmetry, $R(A_2)$ and $R(E)$ being the individual components, and their sum $R(T_1)$ expressing the common octahedral parentage.

The calculated rotational strengths of complex (2), while correct in sign, are less satisfactory quantitatively (Table) than the corresponding values reported [1] for the series of chiral tris(diamine)cobalt(III) complexes. In particular, the sum of the component rotational strengths, $R(T_1)$, determined experimentally from the corresponding c.d. band area of the randomly orientated complex ion, is notably underestimated. A ligand-



(3)

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

polarisation calculation, using the previous parameterisation,[1,5] of the first-order rotational strengths for the recently reported[8] (−)[Co(sep)]$^{3+}$ complex, (−)-{(1,3,-6,8,10,13,16,19-octa-azabicyclo[6.6.6]eicosane)cobalt(III)}, (3), similarly underestimates $R(T_1)$, although giving the correct sign (Table).

The second-order ligand-polarisation treatment of the optical activity of chiral Co^{III}N$_6$ complexes, based upon the mixing of the *d*-electron and the metal–ligand c.t. transitions mediated by the dipoles induced in the ligand groups, requires a knowledge of the polarisation, the dipole strength, and the frequency of each of the c.t. transitions in the far-u.v. region.[1] With the aim of characterising the c.t. transitions of the complex ion in (2), the single-crystal axial c.d. spectrum was measured to the practicable limit of 270 nm at the c.t. band edge, and the solution c.d. spectrum of the corresponding perchlorate salt was carried into the vacuum-u.v. region to the transmission limit of a 10-μm pathlength of D_2O, which is more transparent than water in this region (Figure 1).

The measurements indicate that the lowest-energy charge-transfer c.d. band of the complex ion in (2) at 235 nm in aqueous or methanol solution arises from an $^1A_1 \rightarrow {}^1E$ transition, polarised in the D_3 equatorial plane of the complex, but the polarisations of the second positive c.d. band at 215 nm and of the third band in the c.t. region, negative at 179 nm, remain uncertain. The pattern of the c.d. bands in the c.t. region is less regular for the complex ion in (2) than in the case of the ethylenediamine complex, Λ(+)[Co(en)$_3$]$^{3+}$, where the restricted-sum rule for the rotational strengths of the D_3 components with a common octahedral $^1A_1 \rightarrow {}^1T_1$ ancestry [equation (1)] holds to within *ca.* 10% for both the *d*-electron and the c.t. region.[1]

$$R(A_2) + R(E) = 0 \qquad (1)$$

The characterisation of the E component of the c.t. transition of Λ(+)[Co(en)$_3$]$^{3+}$, through the axial single-crystal c.d. spectrum, allows an assignment of the corresponding A_2 component from the approximate conformity of the vacuum ultraviolet c.d. spectrum to the restricted-sum rule.[1] A similar analysis is not feasible in the case of (2) since there is no obvious pairing of c.d. bands with opposed signs and of comparable magnitudes, approximating to equation (1), in the far-u.v. region (Figure 1). The observed c.t. rotational strengths, from the areas of the c.d. bands at 235, 215, and 179 nm, are 0.38, 0.43 and −0.23 Debye magneton, respectively, for the complex (2) in aqueous solution.

The sensitivity of the c.d. bands of complex ion in (2) in the far-u.v. region to a change of solvent (Figure 1) and to the addition of polarisable anions (Figure 2) raises further uncertainties as to the provenance of these bands. Iodide ions at a concentration of 10^{-4} mol dm^{-3} in aqueous solution enhance the intensity of the positive charge-transfer c.d. bands of the complex by some 30% (Figure 2). Thus the $^1A_1 \rightarrow {}^1E$ polarisation of the c.d. band edge at 270 nm in the single crystal, from the axial c.d. spectrum (Figure 1), may refer to an interionic rather than to an intramolecular c.t. transition in the complex. It is concluded that insufficient data are available at present for the second-order ligand-polarisation treatment of the optical activity exhibited by this complex.

In contrast to the effect of the iodide ion, the multiply charged oxo-anions, phosphate, selenite, and dicarboxylate ions, diminish the intensity of the lowest-energy c.d. band, both in the c.t. and in the *d–d* frequency region of the spectrum of complex (2) in aqueous solution (Figure 2). The reduction in the area of the positive intramolecular charge-transfer c.d. band at 235 nm arises, in the case of the addition of selenite ions, from the overlap with a new negative charge-transfer c.d. in the 280 nm region. The new c.d. absorption has an interionic c.t. character since the intensity of the c.d. band at 280 nm is enhanced both by an increase in selenite concentration and by a reduction in temperature (Figure 2).

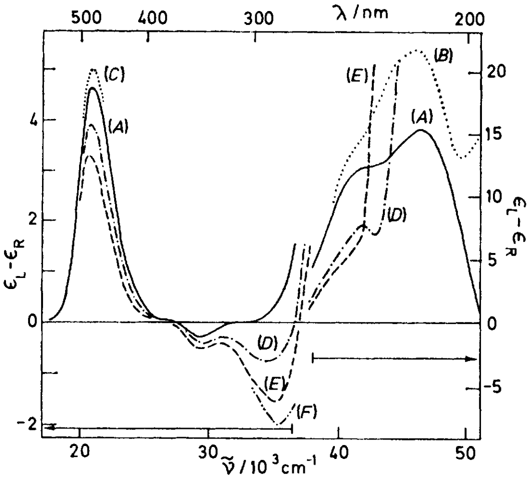
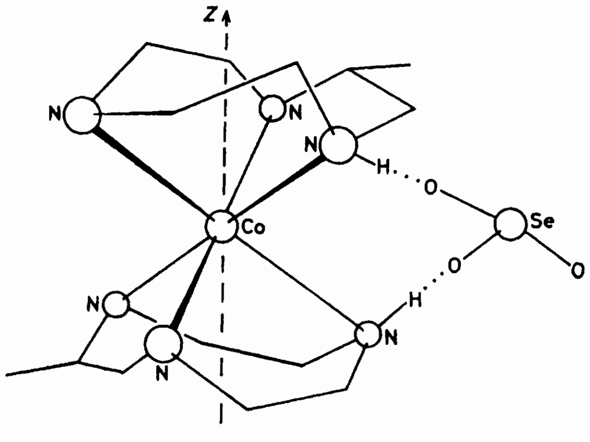


FIGURE 2 The c.d. spectrum in water of [Co{(2R-Me)-tacn}$_2$]-[ClO$_4$]$_3$ (A) and with the addition of 10^{-4} mol dm^{-3} (B) or 10^{-2} mol dm^{-3} iodide (C), or with the addition of 10^{-2} mol dm^{-3} (D) or 0.1 mol dm^{-3} selenite at ambient temperature (E) and at 0 °C (F)

The reduction of the area of the c.d. band in the visible region of the spectrum of complex (2) by the addition of polarisable oxo-anions implies a change in the relative magnitudes of the rotational strengths of the D_3 components of the octahedral $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition, either an enhancement of $R(E)$ or a diminution of $R(A_2)$, or both changes concurrently. Converse changes in the relative magnitudes of $R(A_2)$ and $R(E)$ are produced on ion association by the addition of phosphate or selenite in the series of tris(diamine)cobalt(III) complexes containing five-membered chelate rings.[9] The latter changes in $R(A_2)$ and $R(E)$ are ascribed, in the case of [Co(en)$_3$]$^{3+}$, and the phosphate anion, to the stereospecific formation of an outer-sphere complex or orientated ion pair in which three oxygen atoms of the anion hydrogen-bond to three polar-directed N–H bonds of an exposed triangular face in the co-ordination octahedron, the two ions sharing a common C_3 axis. The structure proposed for the ion pair in solution [9] is supported by the *X*-ray determination of the crystal and molecular structure of $[Co(en)_3]_2[HPO_4]_3{\cdot}9H_2O$, which shows [10] that the anion caps the complex cation by N–H • • • O hydrogen bonding in the solid state.

The covalently capped analogue of $\Lambda(+)[Co(en)_3]^{3+}$ derived from the sexidentate ligand [11] 1,1,1-tris(2′-aminoethylaminomethyl)ethane, and the doubly capped complex [8] $(-)[Co(sep)]^{3+}$ (3), display a similar effect of substitution in the polar spatial regions upon the relative magnitudes of the D_3 component rotational strengths of the $^1A_1 \rightarrow {}^1T_1$ *d*-electron transition of octahedral Co^{III}. The double capping of $\Lambda(+)[Co(en)_3]^{3+}$, by treatment [8] of the complex with aqueous formaldehyde and ammonia to form $(-)[Co(sep)]^{3+}$ (3), changes the overall rotational strength $R(T_1)$ from 0.047 to −0.068 Debye magneton illustrating the general enhancement of $R(A_2)$ at the expense of $R(E)$ by the addition of atoms or groups, whether covalent, ionic, or hydrogen-bonded, to the D_3 polar regions of the $Co^{III}N_6$ cluster.

The contrary enhancement of $R(E)$ at the expense of $R(A_2)$ may be correlated with the location of groups close to the D_3 equatorial plane, whether the groups are covalently bonded, as in the case of the methylene groups in $\Lambda(+)[Co(en)_3]^{3+}$ and analogous 1,2-diamine complexes, or hydrogen-bonded, as is probable from the c.d. changes observed in the visible region (Figure 2) in the ion association (4) formed by oxo-anions with the cation in (2). Molecular models indicate the steric feasibility of bidentate hydrogen bonding (4) between a polyanion in the D_3 equatorial plane and a NH group of the upper and lower ligand (1) in the complex ion of (2), but rule out a polar capping of the complex along the $C_3(Z)$ axis, analogous to the $\Lambda(+)[Co(en)_3][PO_4]$ case.[9]



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An alternative but less-probable origin of the observed c.d. changes in the visible region (Figure 2) is a conformational change in the ligands of the complex ion in (2) on association with an oxo-anion in solution. The c.d. spectrum of the perchlorate salt of (2) in methanol solution over the visible region is invariant with respect to temperature over the range 120—300 K and virtually identical to that of an aqueous solution of the salt at ambient temperature (Figure 1), suggesting that ligand (1) has no significant conformational lability in complex (2). On changing from aqueous to methanol solution a small alteration is found in the c.t. region of the c.d. spectrum (Figure 1), owing possibly to a minor ion pairing of perchlorate with the cation of (2) in methanol.

In the crystal of complex (2) the iodide ions are located [3] on the C_3 axis above the upper and below the lower of the two ligands (1). A similar steric mutual relation between the anion and the cation may persist in the ion-association complex in solution. On the addition of 10^{-2} mol dm^{-3} iodide, the c.d. ($\Delta\varepsilon$) maximum of complex (2) in aqueous solution at 475 nm increases from 4.62 to 4.95, compared with the corresponding c.d. value of 6.07 for the microcrystalline (2) dispersed in a solid matrix of CsCl. Thus for the cation of (2) the component rotational strength $R(A_2)$ is enhanced at the expense of $R(E)$ on ion association with iodide, an observation suggesting a polar location of the perturbing halide close to the C_3 axis of the complex in solution.

EXPERIMENTAL

Preparation.—The ligand (1), (2*R*)-(−)-2-methyl-1,4,7-triazacyclononane and its complex $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]Br_3{\cdot}xH_2O$ were prepared as previously described.[2] Crystals of $[Co\{(2R\text{-}Me)\text{-}tacn\}_2]I_3{\cdot}5H_2O$ (2) were obtained from aqueous solution as thin yellow hexagonal plates. The large hexagonal crystal faces of the main crystal habit were found, by means of a polarising microscope, to be perpendicular to the crystal *c* axis.

Spectra.—These were recorded using Cary 17 (absorption) and Jasco J40C (circular-dichroism) spectrophotometers over the visible and quartz u.v. regions. Both absorption and c.d. spectra in the vacuum u.v. region were obtained with a laboratory-constructed spectrophotometer. The performance of the instrument has been improved, since the original description,[12] by replacing the Rochon MgF_2 polarising prism (length 50 mm) by a shorter (12 mm) Wollaston analogue, in order to enhance transmission at the shorter wavelengths, and the use of a split-head Morvue modulator with a CaF_2 optical element, which eliminates the necessity of nitrogen or helium flushing in the modulator and sample chambers.

Crystals of complex (2) with hexagonal faces 4 × 4 mm in cross-section were polished down to a thickness of 0.04 mm, measured with a microscope fitted with a vernier scale, such that the optical density of the crystal was approximately unity at the visible band maximum (462 nm). The c.d. spectrum of the crystal mounted over an adjustable aperture was recorded for a series of angular increments (30°) of rotation of the sample around the direction of propagation of the radiation along the crystal *c* axis. The c.d. spectrum was found to be invariant with respect to the rotation of the crystal. The experimental rotational strength $R(E)$ recorded (Table), obtained from the directly measured axial single-crystal c.d. spectrum (Figure 1), includes the factor of 2/3 to allow for the locked orientation of the complex in the crystal with respect to the radiation propagated along the crystal *c* axis.

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